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(54) Title: DRIP RESISTANT POLYMER COMPOSITION

(57) Abstract: This invention relates to thermoplastic polymer compositions comprising a clay having drip resistance in the Under-  
writers Laboratories Standard 94 flammability test.

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## DRIP RESISTANT POLYMER COMPOSITION

This invention relates to polymer compositions having drip resistant properties, and more particularly to thermoplastic compositions comprising a clay having drip resistance in the Underwriters Laboratories Standard 94 flammability test.

5 Improvement of the fire resistance or ignition resistance properties of polymers has long been a goal of polymer compounders. Ignition resistance is typically evaluated by the Underwriters Laboratories Standard 94 (UL 94, ASTM procedure D 3801). In this test, two characteristics of the polymer are evaluated, the length of flaming combustion following the application of a test flame and, once exposed to the test flame, the ability of the polymer to  
10 maintain its physical integrity, in other words whether the specimen drips or not.

Different polymers have different combustion mechanisms which require different approaches to impart ignition resistance. Typically, flaming resistance is imparted to thermoplastic polymers by compounds that act as free radical scavenger in the gas phase to extinguish the flame and/or compounds that promote charring to reduce the amount of  
15 available combustible fuel. Examples of free radical scavengers are halogenated hydrocarbons, preferably chlorinated and most preferably brominated hydrocarbons and phosphorous containing compounds, preferably organophosphates. Often, compounds that synergistically improve the effectiveness of the free radical scavengers are used, for example antimony oxide. The most common char promoters are phosphorous containing  
20 compounds and metal salts, such as alkali metal salts of sulfur containing compounds.

The most common drip suppressant used in thermoplastic polymers is tetrafluoroethylene polymers, such polymers are sometimes referred to as polytetrafluoroethylene (PTFE) or Teflon and are disclosed for example in US-A-3,005,795, US-A-3,671,487 and US-A-4,463,130. Preferably, the tetrafluoroethylene polymers form a  
25 fibril structure to stabilize the thermoplastic polymer under molten conditions. Most desirably the tetrafluoroethylene polymers have a high elastic memory. An effective amount of PTFE polymer to impart drip resistance is usually in the range of 0.01 to 5 weight percent of the total thermoplastic polymer composition. Unfortunately, such compounds have significant drawbacks. The elastic memory, and thus the effectiveness as a  
30 drip suppressant, of such compounds is a function of the thermoplastic polymer composition's heat and processing history. Often, thermoplastics containing PTFE polymers lose their drip suppressant characteristics if they are reground or recycled. Further, PTFE compounds can detrimentally effect the physical and flammability properties

of thermoplastic compositions. For example, see WO 99/43747 which shows that antimony free thermoplastic polymer blends compositions with a PFTE polymer containing an organophosphate as the sole flame retardant agent and a synergistic amount of an organoclay demonstrate degraded flame retardant properties as compared to similar compositions without the PFTE polymer. It is well known that PFTE compounds can adversely effect the impact resistance of thermoplastic compositions, specifically the notched Izod impact strength. Additionally, PFTE polymers can cause unacceptable blemishes on the surface of the final molded articles.

PFTE free thermoplastic compositions are known. For example, see US-A-4,582,866 which teaches a multi-block copolyester elastomer composition containing a bromine-containing flame retardant, antimony oxide and an organoclay. While these compositions obtain the V-0 rating some specimens still exhibited dripping during in the UL 94 flammability test. EP 132,228 disclosed a reinforced polyester composition with up to 50 weight percent filler, a flame retardant additive, an organoclay and an alkali metal salt of an aliphatic monocarboxylic acid, but such high levels of filler can negatively effect physical properties, in particular impact strength. The present invention addresses these problems.

Accordingly, the present invention is directed to a thermoplastic polymer composition comprising an effective amount of clay to improve the drip resistance of the thermoplastic polymer in the UL 94 flammability test. Preferably, the thermoplastic polymer is a polypropylene, polycarbonate, polystyrene, polyester, ABS, nylon or thermoplastic polyurethane and the clay is an organoclay.

In a further embodiment, the present invention involves a method for preparing the drip resistant thermoplastic polymer composition described hereinabove.

In yet a further embodiment, the present invention involves a method for producing a molded or extruded article of the drip resistant thermoplastic polymer composition described hereinabove.

In yet a further embodiment, the present invention involves the drip resistant thermoplastic polymer composition described hereinabove in the form of a molded or extruded article.

Component (a) in the polymer composition of the present invention is a thermoplastic polymer. The thermoplastic polymers can be homopolymers or copolymers. Preferably, the thermoplastic polymer which is beneficially drip resistant modified by the

addition of clay can be a polyolefin, a polycarbonate (PC), a polystyrene (PS), a polyester, an acrylonitrile, butadiene and styrene copolymer (ABS), a nylon, a thermoplastic polyurethanes (TPU, for example, PELLATHANE™ or ISOPLAST™ made by The Dow Chemical Company), and blends thereof. Generally the polyolefin polymers which are most frequently used are polyethylene (PE) and polypropylene (PP) made by conventional Ziegler-Natta or metallocene catalysts.

The polypropylene suitable for use in this invention is well known in the literature and can be prepared by known techniques. In general, the polypropylene is in the isotatic form of homopolymer polypropylene, although other forms of polypropylene can also be used (for example, syndiotatic or atatic). Polypropylene impact copolymers (for example, those wherein a secondary copolymerization step reacting ethylene with the propylene is employed), however, can also be used in the polymer compositions disclosed herein. A complete discussion of various polypropylene polymers is contained in *Modern Plastics Encyclopedia/89*, mid October 1988 Issue, Volume 65, Number 11, pp. 86-92. The molecular weight of the polypropylene for use in the present invention is conveniently indicated using a melt flow measurement, sometimes referred to as melt flow rate (MFR) or melt index (MI), according to ASTM D 1238, under conditions of 230°C at an applied load of 2.16 kilogram (kg). Melt flow rate is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt flow rate, although the relationship is not linear. The melt flow rate for the polypropylene useful herein is generally greater than 0.1 grams per 10 minutes (g/10 min), preferably greater than 0.5 g/10 min, more preferably greater than 1 g/10 min, and even more preferably greater than 10 g/10 min. The melt flow rate for the polypropylene useful herein is generally less than 100 g/10 min, preferably less than 75 g/10 min, more preferably less than 60 g/10 min, and more preferably less than 50 g/10 min.

Component (b) in the compositions of this invention is a clay. The clays best suited for use are hydrous alumino silicate-type compounds, generally represented by the formula:



Preferably, the clay is an organoclay. As used herein, organoclay means a layered clay, derived from a layered mineral and in which organic moieties have been chemically incorporated, ordinarily by ion exchange and especially cation exchange with organic ions and/or onium compounds. More preferably, the organoclay is the reaction product

of at least one quaternary ammonium salt with a smectite-type clay having an ion exchange capacity of at least 75 milliequivalents per 100 gram (meq/100 g) of clay, the quaternary ammonium salts having the formula



Wherein  $M^-$  is selected from the group consisting of chloride, bromide, iodide, nitrite, hydroxide, acetate, methyl sulfate and mixture thereof, wherein  $R_1$  is an alkyl group having 12 to 22 carbon atoms and wherein  $R_2$ ,  $R_3$  and  $R_4$  are selected from the group consisting of hydrogen, alkyl groups containing 1 to 22 carbon atoms, aryl groups and aralkyl groups containing 1 to 22 carbon atoms in the alkyl chain.

Smectite-type clays which are useful in preparing the required organoclays include bentonite, montmorillonite, hectorite, and saponite clays with bentonite and hectorite clays being preferred. The clays should have an ion exchange capacity of at least 75 meq/100 g of clay and preferably at least 95 meq/100 g of clay. Useful quaternary ammonium salts for modifying the clay by ion exchange must contain a cation having at least one long chain alkyl substitute having 12 to 22 carbon atoms. For reasons of economy most commercially available useful quaternary ammonium salts have one or more alkyl groups derived from hydrogenated tallow which is principally an octadecyl group. The preferred anion is the chloride ion. Representative quaternary ammonium salts which are useful in preparing the organoclays required by the present invention include methyl benzyl di(hydrogenated tallow) ammonium chloride, dimethyl benzyl di(hydrogenated tallow) ammonium chloride, dimethyl di(hydrogenated tallow) ammonium chloride, methyl tri(hydrogenated tallow) ammonium chloride, and benzyl tri(hydrogenated tallow) ammonium chloride. An especially preferred organoclay is CLAYTONE<sup>TM</sup> HY, a montmorillonite cation exchanged with diethyl di(hydrogenated tallow) ammonium ion available from Southern Clay Products, and montmorillonite cation exchanged with such ions as dodecylimidazolium, trimethyldodecylimidazolium, N,N'-dodecylimidazolium, N,N'-ditetradecylbenzimidazolium or methyl bis(hydroxyethyl)-(hydrogenated tallow) ammonium.

The organoclays are present in an effective amount to improve the drip resistance

of the thermoplastic polymer in the UL 94 test. Generally, the organoclay is present in an amount equal to or greater than 0.01 part by weight based on the weight of the polymer composition, preferably equal to or greater than 0.1 part by weight, more preferably equal to or greater than 1 part by weight, even more preferably equal to or greater than 2 parts by weight, and most preferably equal to or greater than 5 parts by weight based on the weight of the polymer composition. Generally, the organoclay is present in an amount less than or equal to 35 weight percent based on the weight of the polymer composition, preferably less than or equal to 25 parts by weight, more preferably less than or equal to 15 parts by weight, even more preferably less than or equal to 10 parts by weight, and most preferably less than or equal to 5 parts by weight based on the weight of the polymer composition.

Further, the claimed polymer compositions may also optionally contain one or more additives that are commonly used in polymer compositions of this type. Preferred additives of this type include, but are not limited to: impact modifiers such as, but not limited to core-shell graft copolymers; fillers, such as, but not limited to talc, mica, wollastonite, glass or a mixture thereof; ignition resistance additives; slip agents, such as of erucamide, oleamide, linoleamide, or stearamide; mineral oils; stabilizers, such as heat stabilizers, light stabilizers, ultra violet stabilizers; colorants; antioxidants; antistats; flow enhancers; mold releases, such as metal stearates (for example, calcium stearate, magnesium stearate); nucleating agents, including clarifying agents, etc. Preferred examples of additives are ignition resistance additives, such as, but not limited to halogenated hydrocarbons, halogenated carbonate oligomers, halogenated diglycidyl ethers, organophosphorous compounds, fluorinated olefins, antimony oxide and metal salts of aromatic sulfur, or a mixture thereof may be used.

If used, such additives may be present in an amount from at least 0.01 parts, preferably at least 0.1 parts, more preferably at least 1 parts, more preferably at least 2 parts and most preferably at least 5 parts by weight based on the total weight of the polymer composition. Generally, the additive is present in an amount less than or equal to 25 parts, preferably less than or equal to 20 parts, more preferably less than or equal to 15 parts, more preferably less than or equal to 12 parts, and most preferably less than or equal to 10 parts by weight based on the total weight of the polymer composition.

Preparation of the polymer compositions of this invention can be accomplished by any suitable mixing means known in the art, including dry blending the individual

components and subsequently melt mixing, either directly in the extruder used to make the finished article, or pre-mixing in a separate extruder (for example, a Banbury mixer). Dry blends of the compositions can also be directly injection molded without pre-melt mixing.

The polymer compositions of the present invention are thermoplastic. When softened or melted by the application of heat, the polymer compositions of this invention can be formed or molded using conventional techniques such as compression molding, injection molding, gas assisted injection molding, calendering, vacuum forming, thermoforming, extrusion and/or blow molding, alone or in combination. The polymer compositions can also be formed, spun, or drawn into films, fibers, multi-layer laminates or extruded sheets, or can be compounded with one or more organic or inorganic substances, on any machine suitable for such purpose. The polymer compositions of the present invention are preferably injection molded. Some of the fabricated articles include information technology equipment housings, for example housings for monitors, central processing units, printers, etc.; copier covers; keyboards; hand held communication devices, such as pagers, cellular phones, hand held computers, etc.; electronic equipment housings; network interface housings; plenums; and television cabinets.

To illustrate the practice of this invention, examples of the preferred embodiments are set forth below. However, these examples do not in any manner restrict the scope of this invention.

## EXAMPLES

The compositions of Examples 1 to 8 and Comparative Examples A to G were prepared by mixing the dry components and then feeding the dry-blended formulation through a 30 millimeter ("mm") Werner and Pfleider twin screw extruder. Typical compounding conditions on the Werner and Pfleider extruder were: Barrel temperature profile: 220 to 230 °C; Melt temperature: 225 to 230 °C; RPM: 250; Torque: 70 to 80 percent; and Feed rate: 50 pounds per hour. The extrudate is cooled in the form of strands and comminuted as pellets. The pellets were used to prepare 5 by 0.5 by 0.062 inch test specimens on a 70 ton Arburg injection molding machine, typical molding conditions were: Barrel temperature: 220 °C; Mold temperature: 40 °C; Injection pressure: 40 to 50 bar; Holding pressure: 35 bar; Screw speed: 2; Injection speed: 2; Cycle time: 30 seconds; Cooling time: 15 seconds; and Dosage: 12.5.

The formulation content and drip resistant performance of Examples 1 to 8 and Comparative Examples A to G are given in Table 1 below in parts by weight of the total composition. In Table 1:

“PP” is a commercially available homopolymer of polypropylene available having a MFR of 1 under conditions of 230 °C/2.16 kg available from Montell;

“ABS” is a commercially available acrylonitrile, butadiene and styrene copolymer available as MAGNUM<sup>TM</sup> F-430 from The Dow Chemical Company;

“PS” is a commercially available high impact polystyrene available as STYRON<sup>TM</sup> 220 from The Dow Chemical Company;

“TPU” is a commercially available thermoplastic urethane available as PELLETHANE 2103-80 AE from The Dow Chemical Company;

“Clay” is a commercially available montmorillonite cation exchanged with diethyl di(hydrogenated tallow) ammonium ion available as CLAYTONE HY from Southern Clay Products;

“Talc” is a commercially available mineral talc having a maximum particle size of 10 micrometer and a weight average diameter of 1.0 micrometer available as TALCRON<sup>TM</sup> MP-10-52 from Specialty Minerals, Inc.;

“BT-93” is a commercially available ethylene bis-tetrabromophthalimide available as SAYTEX<sup>TM</sup> BT-93 from Albemarle Corporation;

“Deca” is a commercially available decabromodiphenyloxide available as SAYTEX 102 from Albemarle Corporation;

“Sb” is a commercially available antimony oxide available as FIRESHIELD<sup>TM</sup> H from Laurel Industries, Inc., and

“UL 94” is the Underwriters Laboratories standard 94 vertical flame test (ASTM 3801), test specimens were 0.062 inches thick.



Table I

Example Comparative Example COMPOSITION	A	B	C	D	E	1	2	3	4	5	6	7	F	G	8
PP	100	75	90	62	62	90	65	62							
PS									90	95					
ABS											90	95			
TPU													100	90	90
Clay						10	10	10	10	5	10	5			10
Talc			10	10	10									10	
BT-93		20		21			20								
Deca					21			2							
								1							
Sb		5		7	7		5	7							
UL 94, 0.062 in.															
Rating	NR	V-2	NR	V-1	V-2	NR	V-0	V-0	NR	NR	NR	NR	NA	NA	NA
Flaming Drips	yes	yes	yes	no	yes	no	no	no	no	no	no	no	yes	yes	no
Time to 1 <sup>st</sup> drip, sec.	NA	NA	12	0	7	0	0	0	0	0	0	0	2	1	0

NR = not rated

NA = not available

CLAIMS:

1. A polymer composition comprising:
  - (a) a thermoplastic polymer and
  - (b) an effective amount of clay to improve the drip resistance of the thermoplastic polymer in the UL 94 flammability test.
2. The composition of Claim 1 wherein the clay is an organoclay.
3. The composition of Claim 2 wherein the organoclay is prepared from a Smectite-type clay selected from the group consisting of bentonite, montmorillonite, hectorite and saponite clays.
4. The composition of Claim 1 wherein the clay is CLAYTONE HY.
5. The composition of Claim 1 wherein the thermoplastic polymer is selected from the group consisting of polyethylene, polypropylene, polycarbonate, polystyrene, polyester, ABS, nylon and thermoplastic polyurethane.
6. The composition of Claim 1 wherein the thermoplastic polymer is polypropylene.
7. The composition of Claim 1 wherein the clay is present in an amount from about 1 percent to about 20 percent by weight of the total composition.
8. The composition of Claim 1 further comprising an effective amount of one or more flame retardant additives to produce a V-0 rating in the UL 94 flammability test.
9. The composition of Claim 8 wherein the flame retardant additives are selected from the group consisting of brominated or chlorinated organic compounds, phosphate-based compounds, antimony compounds, alkali metal salts, alkali metal acids, and fluorine compounds.
10. The composition of Claim 9 free from a tetrafluoroethylene polymer.
11. A method for preparing a polymer composition comprising the step of combining:
  - (a) a thermoplastic polymer and
  - (b) an effective amount of clay to improve the drip resistance of the thermoplastic polymer with regard to UL 94 flammability test.
12. A method for producing a molded or extruded article of a polymer composition comprising the steps of:
  - (1) preparing a propylene polymer composition comprising:
    - (a) a thermoplastic polymer and
    - (b) an effective amount of clay to improve the drip resistance of the thermoplastic polymer with regard to UL 94 flammability test; and
  - (2) molding or extruding said propylene polymer composition into molded or extruded article.

13. The composition of Claim 1 in the form of a molded or extruded article.

**A. CLASSIFICATION OF SUBJECT MATTER**  
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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 118 723 A (BERK LTD) 3 July 1968 (1968-07-03) page 3; table 1 claims 1-8	1-13
X	----- DATABASE WPI Section Ch, Week 198423 Derwent Publications Ltd., London, GB; Class A17, AN 1984-142894 XP002164677 & JP 59 074152 A (CHISSO CORP), 26 April 1984 (1984-04-26) abstract -----	1-13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1118723	A	03-07-1968	NONE	
JP 59074152	A	26-04-1984	JP 1765287 C	11-06-1993
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